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14. ABSTRACT
We developed functionalized aramid nanofiber networks and demonstrated methods to attach these high performance polymer nanofibers to other materials such as metallic nanoparticles. We demonstrated the tunable characteristics of both the hydrolyzed aramid nanostructures and the nanocomposites formed using them. The unique nanofiber / particle interactions lead to simultaneous stiffening, strengthening and toughening of the mechanical response of the nanocomposites. We have made significant advances in our understanding of the mechanics of transmission mitigation through materials with arbitrary constitutive responses (elastic, viscoelastic, elastic-plastic).

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nanocomposites, impulse mitigation, aramid nanofibers

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ONR Final Report

Abstract – The goal of this project was to develop novel nanocomposite materials with attractive properties for blast and ballistic loading applications. We developed functionalized aramid nanofiber networks and demonstrated methods to attach these high performance polymer nanofibers to other materials such as metallic nanoparticles. We demonstrated the tunable characteristics of both the hydrolyzed aramid nanostructures and the nanocomposites formed using them. The unique nanofiber / nanoparticle interactions lead to simultaneous stiffening, strengthening and toughening of the mechanical response of the nanocomposites over nanofiber networks alone.
In an effort to better understand the mechanical requirements of the materials we have been developing for blast mitigation, we examined the mechanics of an impulse wave through materials. As a result, we have recently made some significant advances in our understanding of the mechanics of transmission mitigation through materials with arbitrary constitutive responses (elastic, viscoelastic, elastic-plastic). This has resulted in the development of a rational design approach to manage the impulse energy from blast or ballistic impact and to mitigate the transmission of its harmful components to a vulnerable target (such as a human body or delicate instrumentation). The approach involves the use of materials with currently achievable properties and can, for example, be applied to the current advanced combat helmet (ACH) without sacrificing its ballistic penetration resistance. The general principals we have developed are applicable to the design of the next generation of military helmets, body armors, underbody systems, etc., again, without changing any additional functionalities of these structures.

Technical Accomplishments –

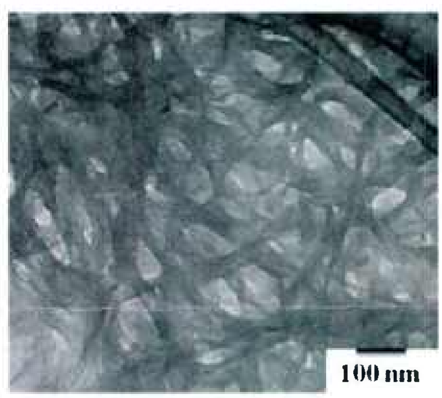

Figure 1: Functionalized aramid nanofibers [4].

- New nanoscale structures for advanced nanocomposites were created from aramid nanofibers by functionalizing them for bonding with other nanostructures or matrix materials. Limitations associated with advanced nanocomposites such as low reactivity and limited variability have been addressed by the creation of functionalized nanometer scale aramid structures, in the form of nanofibers and nanosheets (Figure 1). These were obtained by deprotonating macroscale, commercial Kevlar yarns using potassium hydroxide in dimethyl sulfoxide to yield stable dispersions of nanometer scale aramid fibers that were then hydrolyzed using phosphoric acid (PA). To illustrate the use of these functionally-active nanostructures as building blocks for nanocomposites, they were crosslinked by glutaraldehyde (GA), and formed into macroscopic thin films by vacuum-assisted filtration. It was shown that the mechanical properties of these PA/GA treated films can be tuned by varying the amounts of PA and GA used during synthesis, adjusting the relative amounts of hydrolysis and polymerization. These results are the first demonstration that aramid nanometer-scale fibers can be used to form versatile nanometer sized building blocks that can then be crosslinked to fabricate a wide variety of nanostructured aramid materials with tailorable properties.

- A new family of polymer-matrix nanocomposites reinforced with metal nanoparticles has been developed by combining metallic nanoparticles of gold and copper stabilized by sodium citrate with hydrolyzed aramid nanofibers. Optimal synthesis conditions and constituent parameters resulted in nanocomposites with improved stiffness, strength, and strain-to-failure over hydrogen-bonded aramid networks. The mechanism by which *simultaneous improvements in stiffness, strength and ductility* are realized is attributed to the novel interactions between the aramid fibers and the nanoparticles.

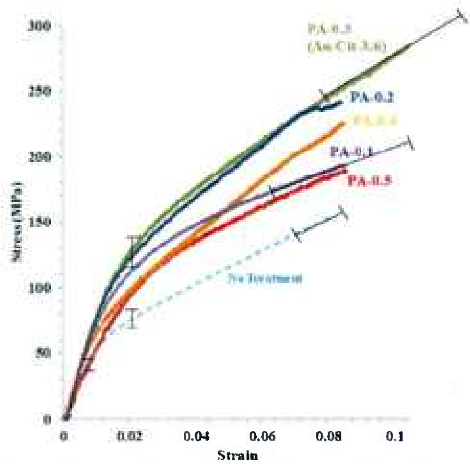

Figure 2: Tunable mechanical properties of metallic nanoparticle reinforced aramid matrix nanocomposites, including simultaneous and significant increases in stiffness, strength, and strain to failure (PA-0.3) over hydrogen bonded aramid networks (No Treatment). [1]

- We have examined the material requirements of an armor system to protect a delicate target from the harmful effects of an impulse delivered to the armor by a blast or impact event. We recently demonstrated that there are two features of the force of a mechanical impact delivered to the target that contribute to its injury – the over-pressure and the impulse. We have shown that measurements of peak target accelerations alone are insufficient to define injurious impacts because they reflect just the over-pressure and do not capture the effects of the impulse. We developed a new design paradigm for impact mitigation involving multi-layering of polymer materials to modulate and optimally dissipate the effects of both of these features. The design strategy requires knowledge of the frequency-dependent response of materials in the kHz-MHz range, a regime that has not been widely explored. The approach requires arranging materials with specific elastic and visco-elastic properties into layers to exploit the high-frequency characteristics of these materials, so as to virtually eliminate the over-pressure and to significantly mitigate the impulse delivered to the target, thereby effectively reducing its deformation and motion relative to surrounding, less delicate structures. While existing armor designs do partially mitigate force transmission, our new design reduces this overpressure by up to an additional order of magnitude over current designs. Furthermore, existing designs do not address impulse mitigation, whereas our new design specifically incorporates features to dissipate energy in an optimal fashion to reduce the impulse. Therefore our new design can easily achieve reductions in over-pressure and impulse by 98% and 80% respectively.

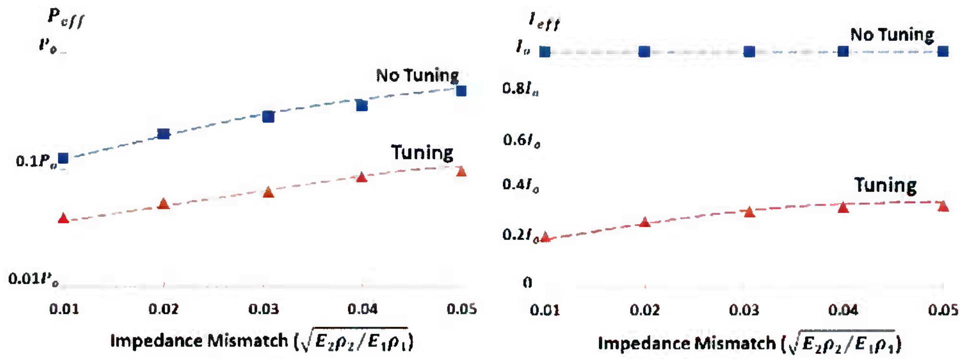

Figure 3: A comparison of the overpressure and impulse mitigation performances of an existing helmet design (No Tuning) vs. our new design (Tuning). [2]

- A comprehensive, finite strain nonlinear viscoplastic constitutive model for a polymer matrix nanocomposite underoing large deformation has been developed and validated against data obtained from polyurethane (PU)-Montmorillonite clay (MTM) nanocomposites. The goal of characterizing the mechanical response under different strain rates and strain amplitudes has been achieved. The model predictions show excellent agreement with experimental results in capturing rate dependent loading/unloading responses for both PU and PU-MTM nanocomposites. The proposed model can easily be extended to characterize other polyurethane based nanocomposites in future work.

Personnel –

PI: Ellen M Arruda

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Undergraduate research assistants: Beverly Chou, David Finkbiner, Jason Francolini, Chris Gannon, Bret Kirchner, John Lavoie-Mayer, Cameron McBride, Carlos Pons Siepermann

Awards –

- Trudy Huebner Service Excellence Award, College of Engineering, University of Michigan, 2014 (Arruda)
- Ann Arbor Spark Best of Boot Camp Award, 2012 (Arruda)
- Ted Kennedy Family Team Excellence Award, College of Engineering, University of Michigan, 2012 (Arruda, Kotov, Waas)

- Excellence in Research Award, American Orthopaedic Society for Sports Medicine, 2012 (Arruda)
- Arthur F. Thurnau Professor, University of Michigan, 2014 (Thouless)
- Ottø Montsted Guest Professorship, Danish Technical University, 2013-2014 (Thouless)
- Fellow, Institute of Materials, Minerals and Mining 2012 (Thouless)
- Vulcans' Teaching Excellence Award, College of Engineering, University of Michigan, 2013 (Thouless)
- Distinguished Faculty Governance Award, University of Michigan, 2012 (Thouless)
- Outstanding Researcher Award (American Society of Composites) – 2013 (Waas)
- Stephen S. Atwood Award, University of Michigan – 2014 (Waas)

Patents –

- Blast/Impact Frequency Tuning and Mitigation, (provisional) November 14, 2013.
- Synthesis and Use of Aramid Nanofibers, June 13, 2012.

Publications –

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2. Rahimzadeh T, Waas AM, Arruda EM, and Thouless MD, "Design of Armor for Protection from Blast and Impact," under review.
3. Yang M, Cao K, Yeom B, Thouless MD, Waas AM, Arruda EM and Kotov NA, "Aramid Nanofiber-Reinforced Transparent Nanocomposites," under review.
4. Cao K, Siepermann CP, Yang M, Waas AM, Kotov NA, Thouless MD and Arruda EM, "Reactive Aramid Nanostructures as High-Performance Polymeric Building Blocks for Advanced Composites" *Advanced Functional Materials*, 23(16): 2072-2080, 2013. DOI: 10.1002.
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7. Li, Y, Waas, AM, and Arruda, EM, "The Effects of the Interphase and Strain Gradients on the Elasticity of LBL Polymer/Clay Nanocomposites," *International J Solids Structures*, **6**: 1044-1053, 2011.
8. Li, Y, Waas, AM, and Arruda, EM, "A Closed-Form, Hierarchical, Multi-Interphase Model for Composites ---Derivation, Verification and Application to Nanocomposites," *Journal of the Mechanics and Physics of Solids*, Vol 59, No 1, pp 43-63, 2011.

9. Kheng E, Iyer HR, Podsiadlo P, Kaushik AK, Kotov NA, Arruda EM and Waas AM, "Fracture Toughness of Exponential Layer-by-Layer Polyurethane/Poly(Acrylic Acid) Films," *Engineering Fracture Mechanics*, Vol 77, pp 3227-3245, 2010.
10. Sain, T., Meaud, J., Yeom, B., Waas, A.M. and Arruda, E.M., Rate Dependent Finite Strain Constitutive Modeling of Polyurethane and Polyurethane-Clay Nanocomposites, Int. J. Solids and Structures, in review, 2014

Presentations

1. Tanaz Rahimzadeh, Anthony Waas, Ellen M Arruda and M. D. Thouless, "A Football Helmet Design Strategy for Concussion Prevention," USNCTAM, East Lansing, MI, USA (June 2014).

2. Tanaz Rahimzadeh, Anthony Waas, Ellen M Arruda, M. D. Thouless, "Design of Materials for Blast-Resistant Armor," 9th International Conference on the Mechanics of Time-Dependent Materials, Montreal, Canada (June 2014).

3. Keqin Cao, Carlos Pons Siepermann, Ming Yang, Anthony M. Waas, Nicholas A. Kotov, M. D. Thouless and Ellen M. Arruda, "Aramid Nanofiber Networks with Tailored Hierarchical Nanostructure," 8th European Solid Mechanics Conference (ESMC) (Graz, Austria, July 9-13, 2012)

4. Keqin Cao, Carlos Pons Siepermann, Ming Yang, Anthony M. Waas, Nicholas A. Kotov, M. D. Thouless and Ellen M. Arruda, " Kevlar-Based Nanocomposites with Hierarchical Structure," *15th European Conference on Composite Materials (ECCM)*, (Venice, Italy, June 24-28, 2012)

5. K. Cao, M. Yang M. D. Thouless, E. M. Arruda, "Kevlar-based Layer-by-layer Nanocomposites," *MRS Spring Meeting* (San Francisco, CA, April 2011).